# New experimental heat capacity and enthalpy of formation of lithium cobalt oxide

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## ABSTRACT

The heat capacity of $LiCoO_2$ (O3-phase), constituent material in cathodes for lithium-ion batteries, was measured using two differential scanning calorimeters over the temperature range from (160 to 953) K (continuous method). As an alternative, the discontinuous method was employed over the temperature range from (493 to 693) K using a third calorimeter. Based on the results obtained, the enthalpy increment of $LiCoO_2$ was derived from $T = 298.15$ K up to 974.15 K. Very good agreement was obtained between the derived enthalpy increment and our independent measurements of enthalpy increment using transposed temperature drop calorimetry at 974.15 K. In addition, values of the enthalpy of formation of $LiCoO_2$ from the constituent oxides and elements were assessed based on measurements of enthalpy of dissolution using high temperature oxide melt drop solution calorimetry. The high temperature values obtained by these measurements are key input data in safety analysis and optimisation of the battery management systems which accounts for possible thermal runaway events.

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## 1. Introduction

Lithium-ion batteries are presently used as power sources in energy storage applications due to the adapted functionality and chemistry for a long cycle life-time, high energy density and high power density. The main challenge not only for electric vehicles but also for smaller portable devices as well as high capacity stationary storage facilities is related to safety behaviour under normal and abusive operating conditions. During charge and discharge processes, the electrode materials are reactive with liquid electrolytes due to the lower thermal stability and undergo exothermic reactions. Understanding the heat generation and propagation in lithium-ion batteries and avoiding thermal runaway at high temperature is therefore a critical issue. In an attempt to improve battery safety, electrodes based on lithium metal oxide such as Li(NiMnCo)$O_2$ intercalation materials are among the currently considered cathode options [1]. In order to fully understand the material behaviour within the cell for normal operation and abuse conditions, it is important to investigate the overall cell chemistry and related thermodynamic properties for the end-member compounds and intermediate compositions. One of the end-member compounds of the Li(NiMnCo)$O_2$ solid solution is $LiCoO_2$ which is

the focus of this study. $LiCoO_2$ has been extensively investigated as a major component in positive electrodes since it has been first reported in 1980 [2]. It has been shown that only the layered structure, also known as O3-phase or high-temperature phase (space group R$\bar{3}$m) displays good electrochemical performance [3]. Since cathodes with O3-phase $LiCoO_2$ active material are considered an important component in lithium-ion batteries, only the O3-phase of $LiCoO_2$ is further considered in this work. In addition, $LiCoO_2$ is an end-member of the Li(NiMnCo)$O_2$ solid solution layered compounds.

A systematic development and design of a suitable thermal management process as well as further materials development and design require the knowledge of basic thermodynamic and kinetic data on battery relevant materials. These input data are also essential to optimise the battery management systems (BMS) which are currently being developed to control parameters such as temperature, voltage, current in batteries of high power and energy density [4,5]. Additionally, experimentally determined thermodynamic data, such as heat capacity and enthalpy of formation, are required as input information for the CALPHAD-based modelling and simulation of multi-component systems [6] for lithium-ion batteries.

Values of the heat capacity of stoichiometric $LiCoO_2$ are limited to low temperature ranges, from (13 to 300) K by Kawaji *et al.* [7] using a self-constructed adiabatic calorimeter and from (1.8 to

300) K by Menetrier *et al.* [8] using a relaxation method. Several estimations of the LiCoO$_2$ heat capacity were made by Zhang *et al.* [9] and Abe and Koyama [10] applying the Neumann–Kopp rule [6]. However these results do not describe well the low temperature range. Recently, Emelina *et al.* [11] measured the heat capacity of LiCoO$_2$ by differential scanning calorimetry over the temperature range (180 to 570) K. The $C_{p,m}$ curve shown in this work has an inflection around $T = 298$ K which could not be completely explained. These values [11] and the experimental results on low temperature heat capacity [7,8] were included into the thermodynamic modelling of the LiCoO$_2$–CoO$_2$ pseudo-binary system performed by Chang *et al.* [12] using the CALPHAD approach.

This study presents new values of experimental heat capacity and enthalpy of formation on the O3-phase LiCoO$_2$ cathode material for lithium-ion batteries. The temperature range covered by these measurements is from 160 K up to 953 K using two differential scanning calorimeters (DSC) and the continuous method, thus a greater range than the earlier studies presented above. Furthermore, the heat capacity of the LiCoO$_2$ from $T = (493$ to 693) K was measured with the discontinuous method in order to validate the heat capacities measured using the continuous method. Based on these results, the enthalpy increment of LiCoO$_2$ was derived from $T = 298.15$ K up to 974.15 K and compared to our enthalpy increment independent measurements at $T = 974.15$ K using transposed temperature drop calorimetry, yielding very good agreement. In addition, the enthalpy of dissolution of LiCoO$_2$ in sodium molybdate solution at $T = 974.15$ K was measured using high temperature oxide solution calorimetry. These results were then used to calculate the enthalpies of formation of LiCoO$_2$ from the constituent oxides and elements which are discussed in the context of the available literature data. The high temperature results are key input data in the optimisation of the BMS which accounts possible thermal runaway events and temperatures up to and above 974 K [4,5].

## 2. Sample and experimental methods

### 2.1. Sample characterisation

The LiCoO$_2$ powder samples used in this study were purchased from MTI Corporation, USA [13] and stored in a glove box under argon (mass fraction purity 0.999999, water and oxygen levels each below $0.101 \cdot 10^{-7}$) MPa. The main components and impurities in the sample were identified by inductively coupled optical emission spectrometry analysis (ICP-OES, OPTIMA 4300 DV from Perkin Elmer). About 50 mg of the powder were dissolved in 6 mL hydrochloric acid and 2 mL nitric acid at $T = 353$ K for 12 h in a drying chamber. The analysis of the main components was accomplished with four different calibration solutions and two internal standards (Na, Sc). The two or three major wavelengths of the elements have been used for calculation. The Li/Co ratio was found to be (0.977 ± 0.006), which would correspond to the stoichiometry Li$_x$CoO$_2$, where $x = 0.977$ (the expanded uncertainty $U$ is $U(x) = 0.006$, 0.95 level of confidence, $k = 2$). The total mass fraction of impurities was determined less than $2 \cdot 10^{-4}$ (table 1). The highest amount of impurity was represented by Na (with a mass fraction of $9.3 \cdot 10^{-5}$), followed by Al (with a mass fraction of $6.3 \cdot 10^{-5}$), Fe (with a mass fraction of $4 \cdot 10^{-5}$) and Zr (with a mass fraction of $2.1 \cdot 10^{-5}$).

The room temperature powder X-ray diffraction was performed in a D4 Endeavour diffractometer (Bruker-AXS GmbH, Karlsruhe, Germany) using Cu Kα radiation with an excitation of 40 kV at 40 mA. The diffraction patterns were recorded in the angle range of $0° < 2\theta < 162°$ with a step size increment of $0.02°$ and a collection time of 5 s per step. The phase fractions and the lattice

parameters were determined using Rietveld refinement analysis software TOPAS 4.2 (Bruker, Germany). The mass fraction of LiCoO$_2$ was larger than 0.99, which corresponds very well with the ICP-OES results (table 1). Co$_3$O$_4$ was identified with a mass fraction below 0.01. The lattice parameters of LiCoO$_2$ were determined as $a = 0.28155(2)$ nm, $c = 1.4051(2)$ nm. These parameters are in agreement with the experimental values reported for the O3-phase LiCoO$_2$ which are in the range (0.2814 to 0.2817) nm for $a$-parameter and (1.405 to 1.408) nm for the $c$-parameter [2,3,11,14].

### 2.2. Thermal analysis (TG/DTA)

Differential thermal analysis (DTA) was performed prior to the calorimetric measurements in order to verify the phase stability and quantify the possible thermal reactions occurring in the temperature range of interest. In this study, a high resolution thermal analysis device (Setsys Evolution 2400, Setaram Instrumentation, France) combined with thermogravimetry (TG) was used. The resolution of the instrument is 0.03 μg for the balance and <1 μW for the DTA signal. The TG/DTA was temperature calibrated at heating rates of $5\ K \cdot min^{-1}$ using high purity standard metals such as indium, bismuth, aluminium, silver, gold and nickel (Calibration Set DTA /DSC, Netzsch GmbH, Selb, Germany). The mass fraction purity of the elements is given as 0.99999 for indium, bismuth, aluminium and gold and the purity of silver and nickel is specified as 0.9999.

LiCoO$_2$ samples of approximately 20 mg, in the form of pressed pellets (applied pressure of 700 MPa for 3 mm diameter samples), were used for the measurements. Simultaneous thermal analysis/thermogravimetric analysis were performed using alumina crucibles (100 μL). Measurements were carried out using heating and cooling ramps of $5\ K \cdot min^{-1}$ with a maximum temperature of 1000 K. Both argon (mass fraction purity 0.999999) and a mixture of argon (purity 0.99999) and 20% oxygen (purity 0.99995) with a total gas flow of $20\ mL \cdot min^{-1}$ were used for the measurements.

### 2.3. Differential scanning calorimetry

The measurements of the heat capacity of LiCoO$_2$ were performed using differential scanning calorimetry by both the continuous and discontinuous methods. All measurements were carried out in argon gas flow (mass fraction purity 0.99999).

All heat capacity determinations were carried out according to the "three-step" method [15] which includes:

1. the determination of the heat flow rate of the zero line, using empty sample and reference crucibles of similar weight;
2. the measurement of a reference substance with a known heat capacity placed in the sample crucible;
3. the measurement of the sample for which the heat capacity is to be determined placed in the sample crucible.

It is imperative for this type of determination that the boundary conditions of the measurement system remain the same during all steps. In order to minimise the impact from handling, no changes were made to the reference crucible during all the three steps noted above. Sapphire (NIST-SRM α-aluminium oxide) was chosen as a reference material (table 1) since its heat capacity is well known from $T = (70$ to 2250) K and it is thermodynamically inert (in argon atmosphere) over this temperature range. Temperature calibration was done using high purity standard metals following a similar procedure as described for the thermal analysis section. In addition, sapphire samples were measured in step 3 to account for the systematic deviations in the calorimeters. The uncertainties quoted for the DSC measurements are the expanded uncertainties with 0.95 level of confidence ($k = 2$).